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CARBORANETHIOL-MODIFIED SURFACES OF GOLD COLLOIDS AND FILMS

KARBORANOVÝMI THIOLY MODIFIKOVANÉ POVRCHY ZLATÝCH KOLOIDŮ A FILMŮ

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ABSTRACT

This thesis deals with the preparation and following surface modification of gold colloidal particles and flat films. Four different ortho-carborane thiol derivatives were used to modify the surfaces of gold nanoparticles and flat gold films. The novel materials engendered from these modifications are extraordinarily stable species with surfaces that support self-assembled monolayers of 1-(HS)-1,2-C₂B₁₀H₁₁, 1,2-(HS)₂-1,2-C₂B₁₀H₁₀, 1,12-(HS)₂-1,12-C₂B₁₀H₁₀, and $9,12-(HS)_2-1,2-C_2B_{10}H_{10}$. Characterization of these materials revealed that molecules of the carborane thiol derivatives are incorporated inside the nanoparticles. This structural feature was studied using a number of techniques, including X-ray photoelectron spectroscopy (XPS), UV-Vis and IR spectroscopies. Thermal desorption experiments showed that carborane molecules detach and leave the nanoparticle surface mostly as $1,2-C_2B_{10}H_{10}$ isotopic clusters, leaving sulfur atoms bound to the gold surface. The surfaces of both the gold nanoparticles and the flat gold films are densely packed with carborane thiolate units. One carborane cluster molecule occupies an area of 6-7 surface gold atoms of the nanoparticle and 8 surface gold atoms of the flat film. XPS data showed that molecules of $1,12-(HS)_2-1,12-C_2B_{10}H_{10}$ bind to the flat gold surface with only one half of the thiol groups due to the steric demands of the icosahedral carborane skeleton. Electrochemical measurements indicate complete coverage of the modified gold surfaces with the carborane thiol molecules. Additionally, the preparation of gold single-crystal micro-plates and micro-wires of well developed shapes is described. The geometry of these crystal plates is derived from triangular and hexagonal motifs, and their crystal facets represent naturally grown flat surfaces. The dimensions of the gold micro-plates, ~ 10 - 80 µm, are sufficiently large to enable their easy mechanical manipulation. Atomic force microscopy showed very good flatness of the gold crystal plates and provided a basis for comparison with macroscopic gold films. Following the modification of these gold crystal surfaces with $1,12-(HS)_2-1,12-C_2B_{10}H_{10}$, a monolayer of gold nanoparticles was attached on top of the carborane moieties and a uniform coverage was achieved. Scanning and transmission electron microscopies were used to observe the formation of the monolayer. Gold colloidal particles linked together were prepared and studied in order to visualize the molecular distance of the carborane linker connecting the particles. The chemical composition of the assemblies was studied using X-ray photoelectron spectroscopy.

ABSTRAKT

Tato disertační práce se zabývá přípravou a následnou povrchovou modifikací zlatých koloidních částic a rovných filmů. Čtyři různé thiolové deriváty orto-karboranu byly použity k modifikaci povrchů zlatých nanočástic a rovných zlatých filmů. Tyto nové materiály odvozené od zmíněných modifikací jsou mimořádně stabilní s povrchy, na kterých vznikají samovolně uspořádané monomolekulární vrstvy 1-(HS)-1,2-C₂B₁₀H₁₁, 1,2-(HS)₂-1,2-C₂B₁₀H₁₀, 1,12-(HS)₂-1,12-C₂B₁₀H₁₀, a 9,12-(HS)₂-1,2- $C_2B_{10}H_{10}$. Charakterizace těchto látek vedla k odhalení, že část molekul thiolkarboranů je inkorporována uvnitř připravených koloidních nanočástic. Tento fenomén byl studován řadou experimentálních technik včetně fotoelektronové spektroskopie (XPS) a UV-Vis a IR spektroskopiemi. Experimenty s termální desorpcí ukázaly, že karboranové molekuly unikají z povrchu nanočástic převážně jako $1,2-C_2B_{10}H_{10}$ isotopické klastry a zanechávají na povrchu zlatých nanočástic vázané atomy síry. Povrchy zlatých částic i rovných zlatých povrchů jsou hustě pokryty thioláty karboranů. Jedna karboranová molekula na povrchu zabírá plochu přibližně 6-7 atomů zlata na povrchu nanočástice a 8 atomů zlata na povrchu rovného zlatého filmu. Výsledky z XPS prokázaly, že molekuly $1,12-(HS)_2-1,12-C_2B_{10}H_{10}$ se váží k povrchu pouze jednou polovinou svých thiolových skupin z důvodu prostorových nároků karboranového ikosaedru. Výsledky elektrochemických měření ukazují na kompletní pokrytí zlatých povrchů molekulami thiolových derivátů karboranů. Dále je popsána příprava zlatých mikro-krystalů s tvary destiček, drátků a polyedrů. Geometrie destiček je odvozena od trojúhelníkových a hexagonálních motivů a jejich vnější krystalové plochy představují přirozeně rostlé rovné plochy. Rozměry zlatých mikro-destiček, ~ 10 - 80 µm, jsou dostatečně velké, aby umožnily snadnou mechanickou manipulaci. Mikroskopie atomárních sil ukázala na velmi rovné plochy na povrchu těchto destiček a poskytla základ pro porovnání s makroskopickými zlatými filmy. Modifikace povrchů zlatých krystalů pomocí 1,12-(HS)₂-1,12-C₂B₁₀H₁₀ vedla k následnému připojení monovrstvy zlatých nanočástic s rovnoměrným rozložením na povrchu. Skenovací a transmisní elektronové mikroskopie byly použity na pozorování vzniku těchto monovrstev nanočástic. Zlaté koloidní částice vázané k sobě byly připraveny a studovány z důvodu vizualizace molekulární vzdálenosti dithiolového karboranového linkeru spojujícího obě částice. Chemické složení připravených uspořádáních bylo studováno použitím fotoelektronové spektroskopie.

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CHAPTER ONE INTRODUCTION

1.1 Gold surface modifications, colloids and films

During the last 20-30 years the syntheses and characterizations of gold colloids and gold flat films modified with organic molecules have provided a stimulating challenge to inorganic, physical, and other chemists. However gold colloids are known for centuries. People used them for decorative purposes already in the Roman Empire. In 1665 Andreas Cassius and his son described gold purple, known today as the "*purple of Cassius*".¹ This purple proved to be a tested dye for glass melts. Of course the colloidal character of these gold species was not recognized in that time. Berzelius, a Swedish scientist, regarded it as a chemical compound. In 1856, Michael Faraday wrote a scientific article about gold colloids; "Experimental relation of gold and other metals to light", as was his study entitled, was published in Philosophical Transactions of the Royal Society of London.² Faraday described procedures for the preparation of both gold colloids and gold films in his study. His work is a seminal contribution to this area of chemistry and later after its publishing stimulated further scientific interest in gold colloids. Reinvestigation of Faraday gold colloids was reported previously.³ The preparation of the colloidal gold was based on adding a few drops of a carbon disulphide solution of phosphorus to an aqueous solution of gold trichloride. The mixture was shaken and immediately turned violet which indicates formation of fine particles of gold. At the beginning of the 20th century, Zsigmondy studied heterogeneous properties of colloids.^{4,5,6} He was dealing with the gold purple of Casius and provided a proof for the view which recognizes the mixture as consisting of very fine gold particles and stannic acid. He started to solve the fundamental questions about size and shape of colloidal particles using microscopic techniques and the colloids were described as filaments, lamellae or platelets. Also an aggregation of smaller particles into larger aggregates was observed.⁷ He classified the colloidal solutions as materials that can not be described as suspensions or ordinary solutions and observed a similar behaviour as Berzelius that a colloidal mixture may sometimes behave like a chemical compound.

The increasing tendency to find applications for colloidal materials and surface-modified flat films dictates trends and directions of current research.^{8,9} Small size objects with potential use in nearly the molecular electronics have attracted attention of scientists from a number of scientific areas. Self-assembly processes seem to be very promising especially because they work with a single molecule as a practical limit. Gold is recognized as convenient substrate due to its several

undeniable properties. It is easily available in elemental form and has been largely studied to date. It is resistent toward oxidation when exposed to air. On the contrary, silver and some other metals are cheaper but less inert.¹⁰ Gold films are easy to prepare and are also commercially available.¹¹ Majority of these films are prepared by epitaxial growth of gold on mica or glass. These procedures afford surfaces with large crystalline terraces of about 100 nm in width¹² which are suitable for scanning tunnelling (ST) and atomic force (AF) microscopies. Adhesion of the gold layer to the glass or mica substrate can be improved by pre-deposition of other metals, mostly Ti, Cr or Ni. Migration of these pre-deposited metals through the gold layer toward the surface has been observed.¹³ Proper investigation of thin films require methods typical for surface science. X-ray photoelectron spectroscopy (XPS), attenuated total reflection (ATR) infrared spectroscopy (IR), contact angle measurements represent only small fraction of the existing analytical tools.

1.1.1 Gold colloids are solution-grown crystallites with nanometre dimensions. These materials support self-assembled monolayers of various organic molecules on the surface. The organic molecules form a protecting shell and, thus, avoid aggregation of the colloids. The size of the particles is an important factor which influences their electronic properties.^{14,15} Gold colloidal particles with a limited number of atoms can be regarded as a transitional phase from a single atom to bulk material that consists of many thousands or millions of atoms. Metal character of these species has been the topic of many discussions and reports published in the literature.¹⁶ The colloidal crystallites have face-centred-cubic (fcc) structure and can be easily prepared with various shapes and sizes using numerous techniques.¹⁷⁻¹⁹ These techniques mostly involve reduction of Au³⁺ with diverse reducing agents in the presence of organic surfactants. The colloidal materials are often regarded as potential building blocks for advanced future materials. Examples of more shapesophisticated colloidal particles are nanorods and nanowires,²⁰⁻²² tetrapod branched nanocrystals,^{23,24} nanocubes^{25,26} and polyhedral particles. These inorganic nano-size crystallites can be statistically described with an average and distribution of the diameter. Narrow size distribution is often the desired target of the synthesis. Aside the colloidal particles that still might, more or less, exhibit bulk character there exists a series of molecular gold clusters consisting of an accurate number of gold atoms. These cluster compounds are stabilized mostly by a phosphine shell. Their structures have been determined using X-ray analysis^{27,28,29,30} and are derived from a centred chair $(Au_{12})^{31}$ or a centred icosahedron $(Au_{13})^{32}$ UV-Vis spectra of these specimens consist of several bands that are characteristic of a given number of gold atoms.³³ The electronic structure of these molecular gold clusters can be described by discrete energy levels rather than by a conductive waste as in bulk gold. The density of the electronic states of these size-dependent materials controls many of their physical properties. Despite the fact there are numerous theoretical studies dealing with

conformation of organic-shell-free gold clusters with only a few atoms,³⁴⁻³⁶ the experimental studies of hollow gold cages are very rare. However, a report on their experimental detection appeared recently.³⁷

Precise control of the particle size allows their self-assembly into ordered structures.³⁸ Colloidal particles can be deposited on the substrate surface either by evaporation of their aqueous solution or tethered via functional groups. The latter approach can be realized by self-assembly of bifunctional organic molecules on the substrate surface and subsequent attachment of gold particles to the organic monolayer.^{39,40}

1.1.2 Organic-thiol modified gold films. The preparation of self-assembled monolayers of alkanethiolates on gold by adsorption of di-*n*-alkyl disulphides from their dilute solutions^{41,42} was reported in 1983. Allara and Nuzzo characterized the modified gold films using infrared (IR) spectroscopy, wetting angle and ellipsometry. The measuring of wetting angle generally gives the first information about changes on the surface. Through treatment with suitable species it is possible to change the wetting and adhesion properties of gold surface. The static contact angle of water on bare gold film is approximately 72° .⁴³ The surface of gold film modified with alkanethiols becomes hydrophobic due to non-polar character of the hydrocarbon chains.⁴⁴ The alkanethiol derivatives are generally assumed to bind to gold surface as thiolate species. They form crystallinelike structures with fully extended alkyl chains tilted from the surface normal by 20-30°.45 However, the alkyl chains can occasionally form ball-like structures and thus disorganize large areas of the organic monolayer.⁴⁶ There are two procedures for the preparation of the alkanethiolate monolayers on gold films. The first is the ordinary solution technique, which involves immersion of a gold substrate in the solution of the thiol derivative, and the second, which gives very similar results, is based on exposition of the gold film to vapours of the thiol derivative at ambient or low pressure. The preparation of octanethiol self-assembled monolayers using ambient-pressure vapourphase deposition was described recently.⁴⁷ The vast majority of the surface is densely covered by the thiolate units with hexagonal arrangement. In both cases there was an excess of the thiol derivative during the treatment. However it was reported that the ambient pressure vapour deposition technique afforded larger domains. The organic monolayers can be prepared from solutions containing dialkyl disulphides as well as alkanethiols.⁴⁸ Both species afford indistinguishable results. The organic molecules on the gold surface can be also replaced by another thiol molecules.⁴⁸ Solution replacement of R'-S on gold surface with R-SH is faster then with R-SS-R. This behaviour is explained with different steric demands of alkanethiol and dialkyl disulphide molecules and, therefore, in their different ability to approach the modified surface. The assemblies

of organic thiol molecules were largely studied using X-ray photoelectron spectroscopy. Focus has been given on S 2p region to reveal the chemical character of the sulphur atoms. The value of the binding energy of S 2p electrons for octanethiolate sulphur is 162.0 eV,⁴⁷ which is consistent with the value assigned in the literature to the thiolate form of sulphur atoms. Formation of disulphides with the binding energy of 163.2 eV was reported as a consequence of the X-ray irradiation.^{49,50} The irradiation can also result in CC and CH bond breaking and this process causes disordering of the previously ordered monolayer of alkane chains. Accurate coordination of the thiolate and disulphide molecules to the gold (111) surface was studied using density-functional theory (DFT) calculations⁵¹⁻⁵³ and scanning tunnelling microscope (STM).⁵⁴ Methanethiol derivative became very attractive because its molecule consists of just a few atoms. Other thiol derivatives of organic character that have been studied are e.g. decanethiol,⁵³ biphenylthiol⁵⁵ or 1-adamantanethiol.⁵⁶ The exploitation of the organic self-assembled monolayers for thin film transistors was described recently.⁵⁷ The usage of the organized organic assemblies of very low thickness in electronic devices brings some technical problems. One such problem is the formation of the top metal contact. While the deposition of metals by evaporation onto organic or polymeric films using cover masks to make contacts is common and well mastered technological process,⁵⁸ the deposition of metals onto organic monolayers is very delicate and can fail due to several reasons. The metal atoms may diffuse through the organic layer under the influence of an electric current and form a conductive bypass.^{59,60} This bypass can be formed also during the top contact deposition due to pin holes that might appear in the organic monolayer.

1.2 Alkanethiol versus Carboranethiol derivatives

Carboranethiol derivatives represent inorganic cluster species that do not have any comparable counterparts in organic chemistry. These and other clusters of boron hydrides do not exist in nature. To introduce them properly, it is necessary to briefly mention the fundamentals of boron hydride chemistry.

1.2.1 Boron hydrides are dated to the beginning of the 20th century when A. Stock pioneered new air sensitive techniques and prepared the first BH compounds.⁶¹ One of the first hydrides, with the chemical composition B_2H_6 , called diborane, is the first of the existing members of the homological series of boron hydrides. The simpler borane BH₃ does not exist. Other examples of the species prepared by Stock are e.g. B_4H_{10} , B_5H_9 , B_5H_{11} , B_6H_{10} , B_6H_{12} , $B_{10}H_{14}$. They can be assigned to two general formulas, B_nH_{n+4} and B_nH_{n+6} . The structure of these species was an open question in the time of their discovery. Dilthey proposed the structure of diborane with bridging hydrogen atoms in 1921⁶² and this was confirmed with electron diffraction measurements 30 years later in 1951 by

Hedberg and Schomaker.⁶³ Boron, which is in Mendeleev's periodic table next to carbon, has only three electrons to form bonds. The theoretical description of bonding in boron clusters has started with the concept of the 3-centre 2-electron bond proposed by H. C. Longuet-Higgins in 1949. This concept was used and further explored by W. N. Lipscomb.^{64,65} Geometry of borane clusters can be derived from a regular icosahedron, which is an essential unit in boron chemistry. In 1955, Longuet-Higgins and Roberts worked out the existence of icosahedral boron hydride using molecular calculations.⁶⁶ It can exist only as stable dianion, $B_{12}H_{12}^{2}$. Their predictions were confirmed in 1960 with the preparation⁶⁷ and X-ray analysis⁶⁸ of this dianionic compound. Consequently a series of compounds with a general formula $B_n H_n^{2-}$ was predicted. Examples of these are $B_5H_5^{2-}$, $B_6H_6^{2-}$ or $B_7H_7^{2-}$. A set of electron counting rules that rationalized known boron hydride clusters were proposed by Wade.⁶⁹ These rules helped to predict new structures of boranes, carbaboranes, metallaboranes and others. The main stoicheiometric series of boron clusters were defined as $closo-[B_nH_n]^{2-}$, *nido-B*_nH_{n+4} and *arachno-B*_nH_{n+6}. The bonding in these clusters is described using so called s t y x numbers.⁷⁰ "s" is the number of B-H-B bonds, "t" is the number of three centre BBB bonds, "y" is the number of two centre BB bonds, and "x" is the number of BH₂ groups.

One of the most studied of all polyhedral boron hydride clusters is decaborane, $B_{10}H_{14}$,⁷¹ which has been prepared already by Stock at the beginning of the 20th century. One of the syntheses involves pyrolysis of B_2H_6 at 100-200°C in the presence of catalytic amounts of Lewis bases such as Me₂O. Decaborane is a colourless volatile crystalline solid which reacts with acetylenes to form a neutral and stable icosahedral *closo*-C₂B₁₀H₁₂. This specie is the most studied member of the carborane cluster family.

1.2.2 Carboranes. Boron atoms in the cluster frameworks can be formally replaced by various heteroatoms. The products of this replacement are generally called heteroboranes. Therefore, dicarba-*closo*-dodecaborane clusters are formally made by replacement of two BH⁻ units by isoelectronic CH in the icosahedral $B_{12}H_{12}^{2-}$. This group of icosahedral $C_2B_{10}H_{12}$ molecules, that were described in the literature in 1963,^{72,73} has three isomers; *ortho*-carborane 1,2-C₂B₁₀H₁₂, *meta*-carborane 1,7-C₂B₁₀H₁₂ and *para*-carborane 1,12-C₂B₁₀H₁₂. Figure 1 shows these three isomers of $C_2B_{10}H_{12}$ and indicates equivalent positions/vertices in the cluster frameworks. The carbon atoms have strong electron-withdrawing effect and cause a decrease of electron density by the boron atoms. The relative charges of boron vertices in *ortho*-carborane are the following: the most negative are positions 9 and 12, the intermediate are 4, 5, 7 and 11 and the least negative charge is at positions 3 and 6. For *meta*-carborane the order of decreasing negative charge should be 9, 12 >

5, $12 \approx 4$, 6, 8, 11 > 2, 3. In *para*-carborane, the boron atoms are identical and bear a negative charge.⁷⁴ The accurate charge distributions on the icosahedral carboranes were reported by Lipscomb⁷⁵⁻⁷⁹ 1,2-dicarba-*closo*-dodecaborane posses high inherent dipole moment with the positive part oriented toward the carbon atoms, the vector lies in the C_2 axis.⁸⁰ The value of dipole moment was theoretically predicted to be 4.53 Debye⁸¹ and confirmed by experimental measurements that afforded value of 4.50 Debye⁸² or 4.31 Debye.⁸³⁻⁸⁵ All three isomers are white crystalline solids and are very stable toward heating. The *ortho*-carborane is unaffected below 400 °C, at higher temperature to 500 °C in an inert atmosphere it rearranges quantitatively to *meta*-carborane,⁸⁶⁻⁹¹ and at approximately 620 °C *para*-carborane is formed.



Figure 1. Schematic representation of the three isomers of $C_2B_{10}H_{12}$: *ortho*-carborane, *meta*-carborane and *para*-carborane (from left). Hydrogen atoms at vertices of the carborane icosahedra have been omitted for purposes of clarity. The larger black dots at vertices indicate the positions of carbon atoms.

1.2.3 Carboranethiol derivatives. The hydrogen atoms at vertices of the carborane clusters can be substituted by SH groups to afford carboranthiol derivatives. The electron densities on the skeletal atoms can be qualitatively judged on the basis of comparison of the acidities of the thiol groups placed at various positions.⁹² Also another direct information can be obtained from the binding energies of sulphur atoms measured using X-ray photoelectron spectroscopy.⁹³ The electron-withdrawing effect results in strong acidity of SH groups attached to carbon atoms. Therefore, the C-SH derivatives of *ortho*-carborane have the pK_a value at about 3.0. Thiol derivatives of C₂B₁₀H₁₂ substituted at carbon atoms are prepared mostly by a method which involves metallation followed by treatment with sulphur and acidic hydrolysis. On the contrary the B-SH derivatives with SH groups in positions 9 and 12 have the pK_a value at about 10. These pK_a values underline the very different character of SH groups bound to boron and carbon vertices. Other examples and values are described in the literature.⁹⁴ A series of four different derivatives was used to realize this study. These derivatives are shown in Figure 2 in the Experimental section.

1.3 The scope of the study

This thesis reports a study of both gold colloidal particles and gold flat films modified with carboranethiol molecules. The novel materials engendered from these modifications are characterized using a number of methods which revealed significant differences from the alkanethiol-modified gold surfaces reported previously. On the basis of our investigation we propose a special model for the new nanoparticle species that has some carboranethiol derivatives located inside the metal core as well as on its surface. The gold nanoparticles, which represent a colloidal system, can be viewed as a model for the modified flat films that were investigated for electronic applications exploiting pre-organized mono-layers of compounds with a distinct dipole moment. These monolayers may have interesting properties when used as dielectric layers of very tiny dimensions. Both modified gold colloids and gold films are described in this thesis with respect to their complementary character to each other. The synthesis of micrometer gold single-crystal micro-plates and self-assembly of gold colloidal particles on their facets after previous treatment with an excess of $1,12-(HS)_2-1,12-C_2B_{10}H_{10}$ is also reported. A comparison of the morphology with macroscopic gold coatings is shown.

CHAPTER TWO EXPERIMENTAL

HAuCl₄·3H₂O (99.9 %) was purchased from Aldrich. 1,2-C₂B₁₀H₁₂ (99.0 %) and 1,12-C₂B₁₀H₁₂ (99.0 %) for the synthesis of the thiol derivatives were received from Katchem Ltd. (Czech Republic). NaBH₄ was received from OY Finn. Chem. Ltd. (Finland). Gold (I) sulfide (Au₂S) (99.9 %) was received from Aldrich and gold (III) sulphide (Au₂S₃) (99.99 %) from Alfa Aesar (Germany). All solvents were purchased as analytical grade from Lachema Ltd. (Czech Republic). Toluene was additionally distilled on a Vigreux Column. For UV-Vis measurements methanol of HPLC quality from Aldrich was used. Hydrochloric acid (35% aqueous solution) was received as p.a. grade from Lachema Ltd. (Czech Republic).

2.1 Carboranethiol derivatives. 1-(HS)-1,2-C₂B₁₀H₁₁ (1), 1,2-(HS)₂-1,2-C₂B₁₀H₁₀ (2), 1,12-(HS)₂-1,12-C₂B₁₀H₁₀ (3) and 9,12-(HS)₂-1,2-C₂B₁₀H₁₀ (4) (Figure 2) were prepared according to the procedures reported in the literature.^{94,96,97} All these thiol compounds were purified by both sublimation and crystallization techniques as described in the literature, and were isolated in a crystalline form. All compounds were found to be >98 % pure as verified by the following techniques: nuclear magnetic resonance spectroscopy (¹¹B and ¹H NMR), gas chromatography - mass spectrometry (GC MS), elemental analysis (EA) and induced coupled plasma (ICP) spectrometric analysis.



Figure 2. Schematic representation of the thiol-derivatives of *o*-carborane: 1-(HS)-1,2-C₂B₁₀H₁₁ (1), 1,2-(HS)₂-1,2-C₂B₁₀H₁₀ (2), 1,12-(HS)₂-1,12-C₂B₁₀H₁₀ (3) and 9,12-(HS)₂-1,2-C₂B₁₀H₁₀ (4).

2.2 Self-assembly of the carboranethiol derivatives on gold nanoparticles. The established two phase liquid-liquid method⁹⁸ was used. This method, which generally leads to gold nanoparticles soluble in non-polar environments, was first described in 1994 by Brust, Schiffrin and co-workers.

Preparation: HAuCl₄·3H₂O (355.3 mg; 0.9 mmol) was dissolved in 30 ml of distilled water and added to a vigorously stirred toluene solution (90 ml) of tetraoctylammonium bromide (2.1876 g, 4 mmol). The reaction mixture was stirred for 2 h; all tetrachloroauric anion was transferred into the toluene phase, which subsequently turned a deep red color. o-Carboranethiol derivative (1 or 2) was added in solid form as one portion (for amount see Table 1) followed by the linear addition over 10 minutes of a freshly prepared aqueous solution (20 mL) of sodium tetrahydroborate (378.4 mg, 10 mmol). The toluene phase turned a deep violet colour and gas evolution was observed. The reaction mixture was stirred for 5 h at 30 °C in an oil bath. The toluene phase was separated and the solvent evaporated under reduced pressure until approximately 10 mL of the deep violet coloured mixture remained in the flask. This solution was mixed with methanol (200 mL) and stored in the freezer $(\sim -20 \text{ °C})$ over two nights. During this time a black waxy material precipitated. The excess solvent was decanted and the solid was additionally dried under reduced pressure. The crude product was subsequently dissolved in a small amount of acetone and purified by chromatography on a silica gel column with acetone as the eluting agent. Thus, the tetraoctylammonium bromide, which was used as the transferring reagent, was completely removed from the surface of the gold nanoparticles (Figures 7 and 8 and related discussion). All samples had the appearance of black waxy materials before chromatography and that of a loose black-gold powder after purification. Figure 7 shows the total ion current profile of the desorbing molecules from the crude black waxy product. The MS spectra indicate the presence of both, carboranethiol molecules (top left MS spectrum) and tetraoctylammonium bromide (top right MS spectrum). The latter could be bound to the surface due to electrostatic interaction. The chromatography purification causes complete disappearance of the peaks characteristic of the tetraoctylammonium cleavage pathways. Therefore, all studied samples were firstly purified by chromatography. The smaller the amount of the thiol used in the reaction, the more aureate the appearance of the product observed. Typically 60-80 mg of the pure product was obtained in one batch. The pure products were soluble in acetone and methanol, giving violet coloured colloidal solutions. This procedure failed with 4; under the same conditions only a gold sponge was obtained.

Thiol:	2	2	2	2	2	2	1
M / mg	18.8	46.9	93.8	140.7	187.5	234.4	158.7
M / mmol	0.09	0.23	0.45	0.68	0.9	1.13	0.9
Ratio	1:0.1	1:0.25	1:0.5	1:0.75	1:1	1:1.25	1:1
Product	2- MPCs	2-MPCs	2-MPCs	2-MPCs	2-MPCs	2-MPCs	1-MPCs
designation	(1)	(2)	(3)	(4)	(5)	(6)	(7)

Table 1. Data for the above experimental procedure. M: the amount of the thiol derivative used in the synthesis reaction; Ratio: mole ratio of $HAuCl_4 \cdot 3H_2O$: thiol derivative

2.3 Desorption process. Desorbed samples were prepared by heating MPC materials under vacuum (~ 0.1 Torr) in a heated inlet placed in a GC oven of a GC-MS instrument. For details concerning the GC-MS instrument see "Heated Inlet GC-MS" in General Methods. Desorption process was monitored by MS analysis of the gaseous phase evolving from the samples. The time dependency of the desorption experiments, presented in Figures 7, 8, 9 and 10, was obtained by using the following experimental setup: $35 \,^{\circ}$ C (0 min), linear increase of temperature by 20 °C/min up to 280 °C (12.25 min), 280 °C kept for additional 17.75 min. These desorption conditions were the same for preparation of all desorbed samples. The desorbed species were soluble in acetone and methanol, giving dark violet coloured colloids.

2.4 Preparation of macroscopic gold films. Au films were prepared by the evaporation of gold (99.99 %, Safina Ltd., Czech Republic) onto freshly cleaved mica wafers (1.5×1.5 cm) at a substrate temperature of ~ 300 °C under a vacuum of ~ 3.4×10^{-8} mbar. Gold was evaporated from a resistively heated tungsten boat with a deposition rate of 0.5 Å/s. The thickness of the Au films, monitored with a quartz crystal oscillator, was typically 140 nm. The deposition was carried out in a Pfeiffer PLS 570 high-vacuum evaporator equipped with an oil-free pumping system and a liquid N₂ Meissner trap (with a normal base pressure of about 1×10^{-8} mbar). After deposition, the wafers were left to cool to ~ 30 °C and the vacuum chamber was filled with nitrogen of technical purity. By flame annealing Au (111) terraces can be easily obtained. The following procedure was used: the Au film was placed into the flame until dark red glowing appeared. The film was taken out for ~ 30 s and the whole procedure was repeated three times. The Au-film samples were stored under Argon atmosphere at room temperature for 1 hour before use for further experiments.

For comparison, we also used commercially available gold films from Dr. Dirk Schröer (Arrandee, Werther, Germany). These Au films were ~ 250 nm thick deposited on a borosilicate glass with a

chromium interlayer (~ 2.5 nm) for better adhesion of gold to glass. The flame-annealing was done in the same way as described above.

Using Atomic Force Microscopy (MM AFM, Nanoscope IIIa, Digital Instruments, USA), Au (111) terraces of about 100-200 nm in diameter were observed separated by rough boundaries.

2.5 Self-assembly of the carboranethiol derivatives on flat gold surfaces. There are two procedures that were used to obtain SAMs of the thiol derivatives on Au films. First: The o-carboranethiol derivatives were adsorbed onto the gold flat surface by the immersion of freshly prepared and hydrogen-flame annealed gold coatings in 10 mL of acetone solution of **2** (0.21 g; 10 mmol) for one hour and subsequent multiple rinsing with pure solvent. Second: The freshly prepared hydrogen-flame annealed gold coatings were exposed to vapours of the volatile thiol derivatives **3** or **4** overnight. The excess of the thiol derivative deposited on the Au surface (observed in XP spectra) was removed by rinsing the wafer with pure hexane. The latter procedure eliminates any need for long exposure of the Au film to a solvent and thus significantly reduces adsorption of impurities from the solvent. Additionally, we found that the thiol derivative **3** reacts with acetone solvent to produce undesirable side-products that are organic in composition and that unwantedly adsorb to the Au film.

2.6 Preparation of N(Butyl)₄ [Au(S₂C₂B₁₀H₁₀)₂]. HAuCl₄ · 3 H₂O (0.393 g, 1 mmol) was dissolved in 30 ml of a dichloromethane solution of N(Butyl)₄ Br (0.353 g, 1.1 mmol). The mixture turned red and was stirred for 2 hours. 1,2-(HS)₂-1,2-C₂B₁₀H₁₀ (0.42 g, 2 mmol) was added followed by addition of anhydrous Na₂CO₃ (1 g, 9.5 mmol). The mixture was stirred additionally for an hour, filtered and the solvent was evaporated to dryness. The crude solid product was crystallized from dichloromethane overnight to get 0.3 g of the product (28 % yield to HAuCl₄ · 3 H₂O). ¹¹B {¹H} NMR (CDCl₃): δ -10.13 ppm (B₃, B₆; s), -7.97 (B₄, B₅, B₇, B₁₁; s), -6.75 (B₈, B₁₀; s), -2.21 (B₉, B₁₂; s).

2.7 Preparation of [Au_{11}(PPh_3)_8Cl_2] Cl \cdot 4 CH_2Cl_2. To a vigorously stirred solution of Au(PPh_3)Cl (1 g, 2 mmol) dissolved in acetone was added NaBH₄ (0.76 g, 20 mmol). The mixture was stirred for 6 hours with cooling in ice-water bath. During this time a brown solid precipitated, was filtered off, and washed with acetone (100 ml), methanol (25 ml) and acetone (200 ml). The remaining orange-brown solid was dried in air overnight and crystallized by slow diffusion of hexane to a concentrated CH₂Cl₂ solution of the crude product. 86 mg of red crystals of $[Au_{11}(PPh_3)_8Cl_2]Cl \cdot 4CH_2Cl_2$ were obtained. ³¹P {¹H} NMR (CDCl_3): δ 53.0 ppm (s), relative to external 85% aqueous H₃PO₄. Electro-spray MS (1 mg/ml in MeOH/H₂O 80/20): m/z (relative abundance) 4355 (C₁₄₄H₁₂₀Au₁₁Cl₂P₈, 23), 4084 (25), 3852 (88), 3823 (15), 3587 (55). IR (ZnSe

ATR): v / cm⁻¹ v(CH, Ph) 3042; 1478 m, 1433 s, 1094 s, 1026 m, 996 m, 743 s, 688 vs. Anal. calcd. for C₁₄₈H₁₂₈Au₁₁Cl₁₁P₈ ([Au₁₁(PPh₃)₈Cl₂]Cl · 4CH₂Cl₂, 4711): C, 37.73; H, 2.74; P, 5.26; Found: C, 38.24; H, 2.82; P, 5.48.

2.8 Crystal data and structure refinement for $[Au_{11}(PPh_3)_8Cl_2]Cl \cdot 4CH_2Cl_2$. Crystals suitable for single-crystal X-ray crystallography were obtained *via* the slow diffusion of hexane into a concentrated solution of dichloromethane. Data were collected with a Nonius KappaCCD area detector diffractometer, using a sealed-tube X-ray source; $C_{148}H_{128}Au_{11}Cl_{11}P_8$, M = 4710.85, monoclinic (red needle, 0.26 x 0.22 x 0.03 mm), space group $P2_1/c$, a = 22.5824(4), b = 18.2922(4), c = 34.6063(8) Å, $\beta = 95.9040(10)^\circ$, U = 14219.4(5) Å³, Z = 4, Mo- K_a , $\lambda = 0.71073$ Å, $\mu = 11.647$ mm⁻¹, T = 150(2) K, R1 = 0.065 for 18587 reflections with $I > 2\sigma$ (I) and $wR_2 = 0.1839$ for all 28494 reflections collected; Programs were standard control and collection software for the diffractometer, local programs, and members of the SHELX family.^{99,100} CCDC reference number 269205.

Table 2. Selected intra-molecular connectivities (Å). Central Au atom: Au(11), Peripheral Au atoms: Au(1)-Au(10), N denotes the number of individual connectivities for a given mean

	Mean	Range	Ν
Au(peripheral)-Au(central)	2.69	2.6444(7)-2.7283(9)	10
Peripheral Au-Au	2.95	2.8398(9)- 3.0632(9)	20
Au(peripheral)-P	2.29	2.276(4)- 2.303(4)	8
Au(1)-Cl(1), Au(3)-Cl(3)	2.356(4), 2.359(4)	-	-

The central-to-peripheral gold-gold distances lie in the range 2.60(1)-2.72(1) Å and are significantly shorter than the peripheral gold-gold distances 2.84(1)-3.19(1) Å. The distances found for other gold clusters that contain 11 gold atoms are nearly the same.



Figure 3. The crystallographic structure of $[Au_{11}(PPh_3)_8Cl_2]^+$ cluster cation.

2.9 Preparation of gold single-crystal micro-plates and micro-wires. A modified procedure which is generally referred to as 'poly-ol' was used.^{101,102,103} 3.34 g of PVP and 3.17 g of AuCl₃ were separately dissolved, both in 75 mL of 1,3-propanediol. Dissolution of the PVP required gentle heating. These two solutions were then mixed together, resulting in the precipitation of a yellow solid. With vigorous stirring, this mixture was placed in an oil bath heated to 165 °C. The yellow solid dissolved in ~ 10 minutes to give bright orange solution that was stirred with continuous heating for additional 2 hours. After ~ 30 minutes a suspension of micrometer gold crystals could be observed and the mixture turned a golden colour. Once finished, the oil bath was removed and the mixture stored at room temperature for further use. The gold crystals can be decanted with methanol and, therefore, 1,3-propanediol replaced by a less viscous solvent. SEM investigation revealed that the gold suspension consisted of gold crystal micro-plates (Figure 20A).

The use of a smaller amount of PVP (1.1 g) resulted in the formation of aggregates of gold crystals (Figure 20C). These aggregates additionally contained crystals that are perhaps best described as ~ 2-5 μ m polyhedrons (Figure 20B). Vigorous shaking did not re-disperse the aggregates into separate crystals. The use of a larger amount of PVP (6.68 g) in the reaction did not

have any significant effect on the size of the micro-plates. The use of 1,5-pentanediol solvent instead of 1,3-propanediol led to the formation of a mixture of gold micro-plates and micro-wires (Figure 20E and 20F).

2.10 Self-Assembly processes on the gold crystal facets. One drop of a methanol suspension of the gold crystal micro-plates was placed on a glass slide and the solvent was allowed to evaporate at room temperature. The crystals strongly adhered to the glass surface and were not removable by rinsing in various solvents (e.g. water, methanol, dichloromethane, hexane, acetone). This feature ensured the secure deposition of the crystals on a glass slide and simplified their further treatment. The deposited crystals were further treated as follows: A glass slide with the deposited gold crystals was immersed in a CH₂Cl₂ solution (5 mL) of $1,12-(HS)_2-1,12-C_2B_{10}H_{10}$ (123 mg, 0.6 mmol) for an hour followed by rinsing with an excess of the pure solvent. The sample was dried in a stream of Ar and a drop of gold colloidal solution was placed on the glass slide for 18 hours. The colloidal solution was finally rinsed in an excess of distilled water and dried under Ar. The SE micrograph of the colloids assembled on the surface is shown in Figure 21. AFM pictures of an equivalent sample are shown in Figure 22 (pictures C and D). Both demonstrate the highest coverage density that we achieved (~ 1160 nanoparticles per 1 μm^2).

2.11 Oligomers of the gold colloidal particles linked with 1,12-(HS)_2-1,12-C_2B_{10}H_{10}. $1,12-(HS)_2-1,12-C_2B_{10}H_{10}$ (32 mg, 0.15 mmol) was dissolved in 100 mL of 0.1 M NaOH and further diluted with 1 mM NaOH to the desired concentration of 16.2 pM. 1 ml of this solution was mixed with an equal volume of the colloidal gold solution. The ratio of colloidal gold particles to the dithiol derivative molecules was 10:1. The mixture was stored at ~ 4 °C for 24 hours. Afterward, 1 mL of the mixture was diluted by addition of 4 ml of distilled water and 4 ml of 1,3-propanediol. The final solution was vigorously shaken and centrifuged for 2 hours at 3000 rot/min. Subsequently 1 mL fractions were removed one after another followed by microscopic investigation. The two bottom fractions were enriched for dimers, trimers and tetramers of the gold colloidal particles.

2.12 General Methods.

2.12.1 Microscopic techniques.

Transmission electron microscopy (TEM). TEM images were recorded on a Philips EM 201 with an accelerating voltage of 80 kV. Samples were prepared by dropcasting single drops from a $\sim 1 \text{ mg/mL}$ gold nanoparticle in acetone solution onto standard carbon-coated (20-30 nm) Formvar films on copper grids (600 mesh) followed by evaporation in air. *Process Diffraction* software¹⁰⁴ was used for analyzing selected area electron diffraction patterns. The data were assigned according to the JCPDS PDF-2 database.¹⁰⁵

High resolution transmission electron microscopy (HR TEM). The species were analyzed using JEOL JEM 3010 equipped with a LaB_6 cathode as a source of electrons. TEM operates at accelerating voltage of 300 kV and provides a theoretical resolution of 1.7 Å. The microscope is equipped with CCD GATAN MULTISCAN (model 794) and EDS spectrometer (INCA x-stream module OXFORD). All samples were prepared from a solution. A drop of the solution was applied on carbon-coated grid.

Scanning electron microscopy (SEM). The micrographs were collected with microscope Quanta 200 FEG (FEI, Czech Republic). The microscope is equipped with field emission gun to achieve high resolution. The samples were observed "as received", i.e. without any sputtering and/or surface modification, using secondary electrons (SE) in low-vacuum mode (pressure inside the chamber 50 Pa), using two high voltages (30 kV - better resolution, 10 kV - lower sample damage) and the smallest spot size (to minimize sample damage and maximize resolution). Under these conditions, the gold nanoparticles appear lighter and surface of the gold crystal appear darker on the micrographs.

Atomic force microscopy (AFM). Measurements were performed in the contact mode using a commercial scanning probe microscope, Digital Instruments Nano-Scope III, equipped with a Nanosensors silicon cantilever, typical spring constant 40 N m⁻¹. The scanning was done in a drop of distilled water.

2.12.2 Heated inlet GC-MS. MS experiments were performed on a MAGNUM GC-MS ion trap system (Finnigan MAT, USA). A heated inlet device setting developed by Spectronex AG, Basel, Switzerland, was used (Figure 4). The gaseous desorbed molecules, vaporized in the high temperature environment of the GC oven, were transported into the ion trap by using the pressure gradient between the sample crucible ($\sim 10^{-1}$ Torr) and the ion trap manifold ($\sim 10^{-5}$ Torr). Samples were introduced as solids with typical quantities 15-40 mg. The transfer line was heated to 280 °C. The ion trap operated in electron ionization (EI) mode and was tuned using default software settings (Magnum 2.4, Finnigan MAT) to obtain suitable mass calibrations, filament emission current, multiplier voltage and AGC (Automatic Gain Control) settings. The total loss of mass during desorption experiments was determined using microbalances.



Figure 4. The sample holder in heated inlet GC-MS. ITD: Ion Trap

2.12.3 X-ray photoelectron spectroscopy. The photoelectron spectra were measured using an ESCA 310 (Scienta, Sweden) electron spectrometer equipped with a high-power rotating anode, wide-angle quartz crystal monochromator, and a hemispherical electron analyzer operated in a fixed transmission mode. Al K α radiation was used for electron excitation. All measurements were performed with an electron analyzer pass energy of 300 eV and an analyzer entrance slit of 0.8 mm. With these settings the full-width at half-maximum (FWHM) of Au $4f_{7/2}$ photoemission line of bulk Au standard was 0.65 eV. A drop of the metal colloid solution in acetone was deposited on a clean Cu surface and dried. The spectra were recorded at room temperature. The regions recorded were Au 4f, S 2p, B 1s, C 1s and O 1s. In addition the spectra of the valence electrons were measured. The electron take-off angle was 90 ° with respect to the macroscopic sample surface. The pressure of residual gases in the analyzer chamber during spectra acquisition was typically 6×10^{-10} mbar. The accuracy of the measured electron energies was ± 0.05 eV. The samples were conductive and consequently no surface charging effects were observed in the spectra, the line positions measured with flood gun on and off coincided within experimental error. The measured spectra did not change during X-ray irradiation. The spectra were curve-fitted after subtraction of Shirley background¹⁰⁶ using Gaussian-Lorentzian line shape. The spectra of the S 2p electrons were fitted with a doublet structure with spin-orbit splitting 1.18 eV and intensity ratio $2p_{3/2}$: $2p_{1/2} = 2:1$. Quantification of the elemental concentrations was accomplished by correcting photoelectron peak

intensities for their cross-sections,¹⁰⁷ analyzer transmission function and assuming a homogeneous sample.

2.12.4 UV-Vis and IR spectroscopies.

UV-Vis spectroscopy. The electronic spectra were recorded in 1×1 cm quartz cuvettes using a Perkin-Elmer Lambda PU 8720 spectrometer. Colloidal solutions of 1.5 mg of the sample dissolved in 50 mL of methanol were measured. Fitting of the absorption curves was done using Gauss and asymmetric (Asym2sigma) functions in OriginPro 7 (OriginLab, Northampton, MA, USA). The plasmon band was fitted with an asymmetric function and its maximum was determined from the second derivative of the curve.

Infrared spectroscopy. The IR spectra of 1, 2, 3, 1-MPCs, 2-MPCs and the desorbed samples prepared from 2-MPCs (~ 1.3 mg) were measured in KBr pellets on a Philips Pye Unicam PU 9512 at 4000-200 cm⁻¹. Self assembled monolayers of 2 and 3 on Au-films were measured using specular reflection. These experiments were carried out with an 80 ° fixed angle using a Nicolet Nexus 670 FTIR spectrometer (1024 scans, 2 cm⁻¹ resolution), Thermo Nicolet Corporation, Madison, USA. The background was the bare gold substrate. The results were confirmed by attenuated total reflection (Smart Performer accessory) IR measurements with ZnSe crystal using the same spectrometer.

2.12.5 Electrochemical measurements. Voltammetric curves were obtained using a μ Autolab potentiostat (EcoChemie, the Netherlands). A three-electrode cell was used that consisted of a saturated calomel reference electrode (SCE), Pt-plate counter electrode, and a working electrode. In the case of nanoparticle samples and gold sulphides, the working electrode was a paraffin-impregnated graphite rod and the samples were deposited mechanically on the basal surface of the rod (voltammetry of microparticles); An aqueous solution, deaerated by flushing with N₂ gas, of sodium acetate – acetic acid (total acetate 0.2 M, acetate-to-acetic acid 1:1) was used as the electrolyte. In the case of Au-films (bare or modified with 2, 3 or 4) on mica, the plates were used as a working electrode and they were connected to the potentiostat with a crocodile clip; the measurements were performed in a N₂ (g) flushed - deaerated aqueous solution of K₄[Fe(CN)₆] (1 mM), K₃[Fe(CN)₆] (1 mM), and KCl (100 mM). The scanning was performed from the open-circuit potential toward negative potentials and cycled between -0.5 and +0.8 V/SCE using linear polarization at a scan rate of 100 mV/s.

2.12.6 Elemental analysis. Elemental analysis of the MPC materials was done using an ICP-OES spectrometer, made by Hilger-Thermo Electron Corp., type IRIS Intrepid II XSP, equipped with an

ultrasonic CETAC Inc. nebulizer, model U5000 AT. The measurements were done in axial plasma mode.

2.12.7 Contact angle measurements. Contact angles of water were measured at 22 °C on a CAM-MICRO Contact Angle Meter. The following technique was used: Approximately, a 1 μ L drop of distilled water was formed at the end of a needle attached to a 50 μ L syringe. The needle was lowered until the drop touched the surface, followed by the raising of the needle. The drop detached itself from the needle tip. An average of six measurements of stable static drops was done for a bare gold surface and gold surfaces modified with **2**, **3** and **4**.

CHAPTER THREE RESULTS AND DISCUSSION

3.1 Size of the modified gold nanoparticles. The structural questions that concern the dimensions and elemental composition of modified gold nanoparticles are fundamentally related to the ultimate understanding of these materials. Using the two phase liquid-liquid method a series of nanoparticles with average diameters from 2.8 nm to 12.3 nm (Table 3) was prepared.

Table 3. Characteristics of 2- and 1- Monolayer Protected Clusters. D: average particle diameter with standard deviation in brackets (TEM), N_{Au} : theoretical number of Au atoms in the nanoparticle, Γ : surface fraction of Au atoms, Δm : weight loss during the desorption, λ_{PB} : wavelength at the maximum of the plasmon band

Product	D / nm	N _{Au}	Γ/%	Δm - %	λ_{PB} / nm
2- MPCs (1)	12.3 (2.5)	57 680	15	- ^a	538
2- MPCs (2)	5.2 (1.4)	4 360	33	3.3	539
2- MPCs (3)	4.7 (1.3)	3 220	35	3.9	522
2- MPCs (4)	4.4 (1.2)	2 680	40	4.4	521
2- MPCs (5)	3.7 (1.2)	1 570	45	5.1	520
2- MPCs (6)	2.8 (0.9)	680	60	14.75	516
1-MPCs (7)	4.7 (0.8)	3 220	35	4.8	518

^a The weight loss during the desorption was too small for detection.

The gold cores were modified with **2** and, for comparison, in one case with **1**. TEM investigations provided information about the size distribution of the gold cores (Figure 5) and to follow the dependency of the average core size on the molar ratio HAuCl₄·3H₂O : **2** (Figure 6). It is shown that the average size of the nanoparticles decreases with the increasing amount of the dithiol used in the synthesis. The approximate number of Au atoms per one nanoparticle and the corresponding surface fraction is shown in Table 3. These data were calculated with respect to the idealized spherical geometry of the nanoparticles and assuming that the Au-Au bond distance for bulk gold at ~20 °C is 288 pm,¹⁰⁸ which is in agreement with the calculated distance for the bulk gold based on uniform 12-coordination for the gold atoms. We observed that the studied materials consisted also of some bulky composites which appeared in the desorbed samples, partly due to the larger tendency of the "naked" nanoparticles to aggregate. The electron diffraction patterns characteristic

of polycrystalline nanoparticles (see top left inset in Figure 5) and, on occasions, for microcrystalline parts of the desorbed samples, were observed. The basic analysis of these diffraction patterns were completely in agreement with data for bulk gold in the database.¹⁰⁵ The phenomenon of aggregation of the naked gold clusters is also observed in XP and UV-Vis spectra. This is demonstrated for instance in the XPS spectra of Au (5d6s) electrons in Figure 12. Due to the disproportionately large size of the bulky composites, it would be misguiding to determine the average size of the nanoparticles in the desorbed species and, therefore, we studied these samples from a qualitative point of view only.



Figure 5. TEM picture of the **2**-MPCs (6) with the inset electron diffraction pattern (top left) and histogram showing size distribution of the nanoparticles (bottom right).



Figure 6. The relation between the average particle diameter (D/nm) and the mole ratio 2 : HAuCl₄·3H₂O used in the synthesis reaction.

3.2 Desorption of the molecules from the surface of colloidal particles. We were able to make some qualitative assessments of the desorption process by using an electron ionization mass spectrometric technique. Using this technique we identified the species escaping from the gold surface as $C_2B_{10}H_{10}$ and $C_2B_{10}H_{10}S$. These results indicate that sulphur atoms remain on the gold surface of the desorbed nanoparticles. This feature was later verified in XPS measurements (see Table 4 and 5 and Figure 13). The desorbed samples have a high stability and are re-dissolvable even after several weeks of storage in a dry solid state at room temperature. This high stability can only be rationally explained by the presence of the sulphur atoms that remain on the nanoparticle surface after desorption. Analyses of the time desorption curves for 2-MPCs, made using different concentrations of carboranethiol, revealed either one or two desorption peaks. Figure 8 shows a typical desorption curve with two such peaks (I, II) and respective mass spectra indicating the identity of the molecules escaping from the surface. Fragmentation pathways that are typical of the starting carboranethiol derivatives are observed in both inset spectra. However, the first spectrum, representing molecules escaping from the surface at lower temperature (the first desorption peak), has a dominating isotopic cluster mass-envelope with the most intensive peak at m/z 174, which corresponds to an isotopic form of the $C_2B_{10}H_{10}S^{+}$ radical cation and indicates that some sulphur atoms may also escape from the surface. The second spectrum, which is characteristic of the

molecules that desorb from the surface at higher temperature, exhibits a dominating isotopic cluster mass-envelope with the most intensive peak at m/z 142, which belongs to an isotopic form of the $C_2B_{10}H_{10}^{*+}$ radical cation. Notably, the higher-mass fragment desorbs from the surface at lower temperature. Further investigations revealed that the time desorption curves depend on size of the nanoparticles. In a series of experiments, in which the mole ratio $HAuCl_4 \cdot 3H_2O$: 2 was in the range from 1:0.1 to 1:1.1, only the second desorption peak (II) was observed. When the ratio was bigger than 1:1.1 the first peak (I) appeared in the spectra and grew in intensity as the amount of 2 increased. This trend is illustrated in Figure 9 which shows three desorption curves. These results suggest that at a limiting excess of 2 over Au, the carborane dithiol is bound to the gold surface by just one B-S-Au interaction, the second B-S-H remaining free. On desorption, this semi-bonded dithiol escapes as the C₂B₁₀H₁₀S moiety (the first peak), whereas the second peak corresponds to the doubly bounded **2**, which is desorbed as $C_2B_{10}H_{10}$ ("carboryne"). This hypothesis also explains why the heavier C₂B₁₀H₁₀S cluster detaches from the gold surface at a lower desorption temperature, and its prevalence at higher ratios of 2: Au. Further evidence supporting this hypothesis is in the fact that the mono-thiol derivative 1 is desorbed from the 1-MPC material surface just as a $C_2B_{10}H_{10}$ moiety at the same temperature as the first desorption peak for 2-MPCs.



Figure 7. Total ion current profile of the desorbing molecules from 2-MPCs before chromatography purification (see Exp. sec., pages 12 nad 13), obtained with a temperature program starting at 35 °C (0 min) followed by 20 °C/min increase to 280 °C (12.25 min), where it was held to the end of analysis.



Figure 8. Total ion current profile of the desorbing molecules from **2**-MPCs, obtained with a temperature program starting at 35 °C (0 min) followed by 20 °C/min increase to 280 °C (12.25 min), where it was held to the end of analysis.



Figure 9. Desorption curves of samples obtained in the synthesis reaction with the mole ratio $HAuCl_4 \cdot 3H_2O : 2$ (a) 1:0.1-1.1, (b) 1:1.15 and (c) 1:1.35.



Figure 10. (A) Total ion current profile of the desorbing molecules from the nanoparticle surface stabilized by methanethiol. The mass spectrum indicates species that escape from the surface at 185 °C. (B) Extracted profile for the ion-radical m/z = 94.

Methanethiol stabilized gold particles were prepared for comparison. Figure 10 shows that the methanethiolate species escape from the surface as dimethyldisulphide molecules. Therefore, these molecules do not leave sulphur atoms on the surface as carboranethiol derivatives. Also the desorbing temperature is lower by approximately 35 °C.

The loss of mass during the desorption experiments is a good indicator of the amount of carboranethiol clusters on the gold surface. A complete set of desorption data is presented in Table 3. The large amount of carborane and carboranethiolate fragments detected after desorption implies that the surfaces of the gold nanoparticles are densely covered by carboranethiol molecules. Simple calculations, with respect to the average size of the nanoparticles and the desorbed mass, show that approximately 6-7 surface Au atoms are occupied by one molecule of **2**. In this context we are able to evaluate the extent to which the curved gold surfaces of the MPCs imitate the properties of the flat gold surfaces of the SAMs. The idealized space filling projection of carboranethiol molecules attached to a flat gold surface demonstrates that one carboranethiol cage

occupies 7 surface gold atoms. Figure 11 is a schematic representing the approximate area of gold surface that is covered per carboranethiol cluster along the Au (111) lattice plane. A hexagonal overlayer (dashed circles) is placed on the gold (111) surface,¹⁰⁹⁻¹¹¹ with one carborane cluster per seven surface gold atoms. Thus, both the hypothetical results for the packing density of carboranethiol molecules on a flat gold surface, and the experimental results for packing on a curved gold surface, are similar. Indeed, it was found that the larger the nanoparticle was, the closer the number of gold surface atoms occupied by one carboranethiol molecule approximated to 7 – the idealized number of atoms for a flat gold surface. It is worthwhile to compare **2**-MPCs (3) with **1**-MPCs (7) where the average diameter of the nanoparticles is the same for both samples (see Table 3) and we may expect approximately the same surface area. The desorbed mass is bigger for **1**-MPCs (7) than for **2**-MPCs (3) (see Table 3), which indicates a generally higher packing density of molecules of **1** on the gold surface. This difference is caused by the dissimilar steric demands of the mono- and dithiol derivatives; dithiol derivative **2** requires more space and hence its surface density is lower.



Figure 11. (a) Idealized space filling schematic of carborane clusters centered on 6-fold surface units of gold atoms. Dimensions: A, ~ 7 Å; B, 2.88 Å. The real geometry of carborane clusters (dashed circles) is approximately that of a regular icosahedron. (b) A side-on view of the carboranethiol molecules bound to the substrate surface via one and two B-S-Au links respectively. Hydrogen atoms associated with the carborane have been omitted for clarity.

3.3 Binding energy of S 2p electrons, XPS results. XPS allowed us to study further the MPCs described above as well as the desorbed samples, and to compare the data with that obtained for

SAMs of the carboranethiol derivatives on surface of flat gold films. There were several features observed in the XPS data, which significantly contributed to our understanding of the MPC materials. To avoid confusion, it is best to discuss the XPS data in two parts; firstly: The MPCs and the desorbed samples, and secondly: The SAMs of **2**, **3** and **4** on flat gold films.

The results from the XPS elemental analysis of the nanoparticle samples are summarized in Table 4. A good agreement between the measured chemical composition of the carboranethiol molecules and its nominal stoichiometry was observed. Conversely, the data obtained for gold do not correspond to the actual number of Au atoms. This is due to the attenuation of the Au 4f photoelectrons in the nanoparticle and adsorbed molecules of the thiol derivatives 2 or 1. The spectra of C 1s electrons are composed of two components; the first belonging to carbon from carborane clusters (C_{CB}), and the second belonging to carbon from hydrocarbon species (C_{HC}), the latter most likely being a manifestation of surface contamination from solvents used in synthesis. The measured core level binding energies and corresponding FWHM are displayed in Table 4. The Au 4f core levels are shifted with respect to the bulk value toward higher binding energy by 0.13eV for the sample with average particle size $d \cong 5$ nm and by 0.19 eV for the sample with $d \approx 2.6$ nm. These shifts can be attributed to modifications of particle electronic structure by size effects¹¹² and by the bonding of a fraction of Au atoms to sulphur. The observed increase in FWHM of the Au 4f_{7/2} line with decreasing particle size is consistent with this explanation. The measured binding energy of S $2p_{3/2}$ electrons, 162.7 ± 0.1 eV is by 0.7 eV higher than the value reported in the literature¹¹³ for alkanethiolates on planar gold surfaces. This indicates lower electron density on S atoms in the thiolate moieties on the gold nanoparticle. A feature located at 167 eV belonging to partially oxidized sulphur was not observed even after a long period of exposure to air. This demonstrates high stability of the prepared MPC materials. In the XPS measurements we observed a surprisingly high amount of carborane molecules that remained associated with the desorbed samples. A peak representing the binding energy of B1s electrons typical for carborane clusters was observed in the spectra of these samples. Taking into account the total loss of the dense carboranethiol coverage from the nanoparticle surface known from the desorption experiments, we reasoned that some molecules of 2 are inside the gold cores. Other methods used to study the desorbed MPC, which are discussed in more detail in subsequent pages, also seem to verify our hypothesis of the location of carboranethiol molecules within the gold cluster. In the desorbed samples of 2-MPCs, in which we expected to find just one type of sulphur atoms corresponding to a form of surface gold sulphide, we found instead two different types. Of these two types, one was the thiolate sulphur of the starting non-desorbed 2-MPCs and the second was shifted towards lower binding energy, indicating a higher negative charge on these atoms (Figure 13-2). We predicted this

second type of sulphur to be observed in the XP spectrum of the desorbed sample as a result of the desorption process and we assigned it to be the sulphur that remains on the surface of the nanoparticles after desorption of the carborane moieties. Comparison of the binding energies, associated with the surface sulphur atoms and sulphur atoms from gold sulphides, did not reveal many similarities. The desorbed samples and gold sulphides differ in electronic structure, which may cause the observed difference in binding energies of S 2p. Nevertheless it occurred to us that further comparison of gold sulphides and the desorbed samples might be helpful and we later revealed very good agreement between Au₂S and the desorbed sample in electrochemical behaviour (see Figure 16). The spectra in the valence band region, which are dominated by emission from Au 5d electrons, and the spectra of $[Au_{11}(PPh_3)_8Cl_2]^+Cl^-$ cluster compound and bulk Au, included for comparison, are displayed in Figure 12. As expected on the basis of the results obtained with supported gold nanoclusters,^{114,115} an observation was made for the colloidal particles of a decrease in the splitting of the Au 5d band as well as the bandwidth with decreasing of the average size of the nanoparticles. It is known¹¹⁶ that the splitting of the Au 5d band, which is equal to 1.4 eV for a free Au atom, increases roughly linearly with the number of atoms in the particle up to 2.9 eV for bulk Au. The other observation in Figure 12 is that heating of the samples results in an increase of both the 5d splitting and the bandwidth, which is indicative of an aggregation of the nanoparticles after desorption.

Table 4. Elemental concentrations as determined from XPS analysis of colloids and Au films modified by carboranethiols (atomic concentrations). D: average particle diameter (TEM), C_{HC} : carbon atoms from hydrocarbons, C_{CB} : carbon atoms from carboranes

Sample	Thiol	В	C _{HC}	C _{CB}	S	Au	0
Colloid, $D = 2.6 \text{ nm}$	2	10	2.9	2.0	2.1	5.3	-
Colloid, $D = 4.7$ nm	1	10	2.0	2.0	1.2	8.2	-
After thermal desorption		10	2.9	1.8	2.5	12.3	1.4
Colloid, $D = 5.2 \text{ nm}$	2	10	4.6	2.2	2.1	8.3	-
After thermal desorption		10	6.8	2.5	2.3	8.8	6.5
Au film	2	10	1.2	3.3*	2.3	70	-
after heating to 200 $^{\rm o}{\rm C}$		10	3.5	2.3	2.1	89	-
after heating to 400 $^{\rm o}{\rm C}$		10	nm	nm	2.2	148	-
Au film	3	10	11.5	3.7*	2.4	103	-
Au film	4	10	6.7	3.4*	1.9	116	-
Au_2S	-	-	-	-	1	2	-

Au ₂ S ₃	-	-	-	-	2.3	2	-

Table 5. Measured core level binding energies and FWHM for colloidal particles and gold films (in eV). D: average particle diameter (TEM)

Sample	Thiol	Au 4f _{7/2}	B 1s	S 2p _{3/2}	C 1s
Colloid, $D = 2.6 \text{ nm}$	2	84.19 (0.95)	188.9 (1.6)	162.8 (1.0)	284.8 (1.0)
					286.3 (1.0)
Colloid, $D = 4.7$ nm	1	84.10 (0.75)	188.6 (1.2)	162.6 (1.1)	284.7 (0.9)
			189.4 (1.2)		286.3 (1.0)
after thermal desorption		84.01(0.71)	189.4 (1.9)	162.3 (1.9)	284.6 (1.5)
			193.2 (1.7)		286.4 (1.5)
Colloid D = 5.2 nm	2	84.13 (0.81)	188.8 (1.6)	162.7 (1.0)	284.5 (1.2)
					286.2 (1.2)
after thermal desorption		84.02 (0.72)	189.0 (1.7)	162.3 (1.7)	284.8 (1.3)
			189.9 (1.7)	163.5 (1.7)	286.4 (1.3)
			193.0 (1.6)		
Au film	2	84.0 (0.7)	188.6 (1.5)	162.2 (1.0)	284.4 (1.1)
					285.9 (1.1)
After heating to 200 °C		84.0 (0.7)	188.5 (1.6)	162.1 (1.3)	284.4 (1.1)
					285.7
					287.0
After heating to 400 °C		84.0 (0.7)	189.4 (1.9)	162.0 (1.5)	nm
			191.5 (1.9)		
Au film	3	84.0 (0.7)	189.2 (1.0)	162.1 (1.1)	284.6 (1.4)
				163.6 (1.1)	286.0 (1.4)
Au film	4	84.0 (0.7)	189.3 (1.6)	161.7 (1.1)	284.5 (1.4)
					286.3 (1.4)
Au_2S	-	84.0 (0.7)	-	162.4 (1.0)	-
Au_2S_3	-	84.0 (0.7)	-	162.7 (1.2)	-

The self-assembled monolayers of the thiol derivatives 2, 3 and 4 on Au films were investigated and compared with each other. The data also offer an opportunity to compare the SAMs with the MPCs. Figure 13 shows the XP spectra of S 2p electrons. The thiolate sulphur atoms of the derivative **4** bound to Au film has a lower binding energy by 0.5 eV than that of the derivative **2**. An explanation of this shift is obvious when considering the electron densities at different vertices of the $1,2-C_2B_{10}H_{12}$ cluster compound. Boron atoms in positions 9 and 12 have considerably higher electron density than carbon vertices 1 and 2. The XP spectrum of S 2p electrons of the **3**-SAM on Au film is composed of two components; one represents the thiolate sulphur atoms that adhere the carborane cluster to the surface, and the second represents the sulphur atoms from free thiol groups. The binding energy of S 2p electrons of the free thiol group is shifted toward higher value by 1.5 eV in comparison to the binding energy of the thiolate sulphur. Comparison of S 2p electron regions of the **2**- and **3**-SAMs is shown in Figure 13, curves 4 and 5. However, the ratio of the two different types of sulphur atoms in **3**-SAM on Au-film is not exactly 1:1 as we expected, but we reproducibly obtained results with the thiolate sulphur dominant. One possible explanation for observing more of the first (thiolate) sulphur is that they adhere to the surface by both sulphur atoms on step edges still respecting the steric demands of the carborane cluster.



Figure 12. Photoelectron spectra of Au (5d6s) electrons for (1) colloid with D = 2.6 nm, (2) D = 5.2 nm, (3) 5.2 nm after thermal desorption, (4) $[Au_{11}(PPh_3)_8Cl_2]^+Cl^-$ cluster compound, (5) bulk Au.



Figure 13. Photoelectron spectra of S (2p) electrons for (1) **2**-MPCs, (2) the desorbed sample, (3) gold (I) sulphide, (4) **2**-SAM on Au film, (5) **3**-SAM on Au film.

Using the equation derived by Carley and Roberts¹¹⁷ we estimated the surface concentration of S atoms from S 2p and Au 4f photoemission peak intensities. In calculations we employed the value of inelastic mean free path of Au 4f electrons calculated according to TPP-2M formula.¹¹⁸ Assuming that the surface density of Au atoms is 1.52×10^{15} /cm² (i.e. close to the value for (111) plane) we obtained a value of 4.0 ± 0.3 for the atomic ratio Au (surface) / S, which is close to our preliminary view on possible arrangement of carboranethiol molecules on flat surface and confirms the density obtained from the desorption experiments.

Elemental analysis of the MPCs and the desorbed species confirmed our hypothesis that some carborane cluster molecules remain inside the nanosize gold clusters of the desorbed samples. Below is an example of the analysis that was characteristic of the studied MPCs and the desorbed samples. It unequivocally confirms the results of XPS analysis, demonstrating a relatively high amount of carborane molecules remaining in the desorbed species. **2-**MPCs (5): Au, 87.2 % (calculated ratio Au:C₂B₁₀H₁₀S₂ \cong 7:1); the desorbed sample: Au, 93.0 % (calculated ratio Au:C₂B₁₀H₁₀S₂ \cong 14:1).

3.4 Plasmon band and bulk character of the colloids. Whereas the two previous techniques (desorption and XPS measurements) represented solid phase investigation, electronic spectroscopy allowed us to probe the properties of our nanoparticle samples when dissolved to colloidal solutions. In all spectra, a broad plasmon band (PB) was observed at approximately 500-560 nm, which is consistent with the previous reports on alkanethiol-protected gold nanoparticles.¹¹⁹⁻¹²² The band is found at about 560 nm for samples with the biggest average size of nanoparticles and shifts to 516 nm as the nanoparticles become smaller. Figure 14 shows the UV-Vis spectra of a methanol solution of **2**, **2**-MPCs (5) and the corresponding desorbed sample. In addition to the PB, the spectrum of **2**-MPCs exhibits two peaks (I, II) in ultraviolet region. The first peak (I) overlaps with the absorption band for the pure dithiol derivative **2**. The second peak (II), which has the same absorption maximum band energy at 270 nm in all of the studied samples, is independent of core dimensions and surface molecules. We assigned this band to absorption by the carborane clusters incorporated inside the gold cores. In consistence with our model, the electronic spectra of the desorbed samples did not exhibit the first band (I), which is caused by the surface carborane molecules.

The UV-Vis spectra are also qualitatively indicative of the core dimensions as has been shown previously in the literature.¹²¹⁻¹²³ The inset in Figure 14 shows that the intensity of the plasmon band is strongly affected by the nanoparticle size. The intensity decreases as the core size decreases which is in agreement with calculations by Mulvaney.¹²³



Figure 14. UV-Vis spectra of methanol solution of (A) 2-MPCs, (B) the corresponding desorbed sample, and (C) the thiol derivative 2. Inset: UV-Vis spectra of methanol solution of 2-MPCs (2), 2-MPCs (4) and 2-MPCs (6).

3.5 Characterization with infrared spectroscopy, B-H stretching vibrations. The IR spectra of borane and carborane cluster molecules show several characteristic features.¹²⁴ Our interest was focused especially on B-H stretching vibrations v_{B-H} that causes a very strong and broad band at approximately 2600 cm⁻¹. The spectra of **1**-MPCs, **2**-MPCs and the desorbed samples exhibit a band at 2564 cm⁻¹. Spectra of the SAMs prepared from **2**, **3** and **4** show the characteristic v_{B-H} at 2585 cm⁻¹, 2617 cm⁻¹ and 2605 cm⁻¹, respectively. The appearance of an obvious band characteristic of B-H stretching vibration in the spectra of the desorbed samples additionally verified the presence of carborane molecules that did not escape during the desorption process.

3.6 Electrochemical characterization. The investigations so far described in this thesis have provided basic structural information on both the gold nanoparticles and the flat gold films modified with carboranethiol derivatives. We have deduced that the gold surfaces are densely covered by carboranethiol molecules. The electrochemistry of these specimens is another useful tool for characterization of the surface behaviour of the species.¹²⁵

The redox properties of the modified gold nanoparticles were investigated using cyclic voltammetry and compared with the starting carboranethiol derivatives. The *o*-carboranethiol derivatives yield chemically irreversible oxidation peaks (Figure 15), probably due to the oxidative degradation of the molecules initiated by oxidation of the thiol groups. The spectra of **1** (A1, B1) and **2** (A2, B2) are dominated by two main oxidation peaks. Conversely the thiol-capped gold nanoparticles do not exhibit any oxidation peaks except for the oxidation of the gold substrate at potentials overlapping with oxygen evolution reaction at > 1 V vs. SCE. These results indicate that the thiol groups are strongly bound to the surface of gold nanoparticles.



Figure 15. Voltammetric curves of 1, 2, and the stabilized gold nanoparticles: 1-MPCs (7) and 2-MPCs (2). The start of scanning is indicated with the cross, the curves are offset for clarity.

Cyclic voltammetric curves of the desorbed samples and gold sulphides (Au_2S and Au_2S_3) were compared and are shown in Figure 16. A very good qualitative agreement was observed between the desorbed sample and gold (I) sulfide (Au_2S). The oxidation peak is bigger in the second scan and shifted toward less positive potential. This unusual feature is typical of both Au_2S and the desorbed sample.



Figure 16. Voltammetric curves of Au₂S₃, Au₂S and desorbed sample.

3.7 Gold films, bare electrode vs. modified with 2, 3 or 4. To investigate the properties of the 2-, **3-** and **4-** covered gold films, $Fe^{3+} \leftrightarrow Fe^{2+} ([Fe(CN)_6]^{3-}, [Fe(CN)_6]^{4-})$ was used as a convenient and reversible redox system.^{45,126-129} The cyclic voltammetric current-potential (i-E) curves are shown in Figure 17. The voltammograms for the gold film protected with 2, 3 or 4 significantly differ from that for bare gold film; the redox currents are much lower. A reduction current was observed for the 2-modified gold wafer that we assigned to be a ferricyanide reduction current. However, we did not observe any corresponding oxidation as in the case of the 3-modified gold wafer. One possible explanation for the appearance of only the reduction current might be the dipolar character of the molecules of 2 bound to the surface, which represent a monolayer of organized dipoles directed from the surface upwards. The more electronegative part of the carborane clusters is around the 9 and 12 BH vertices. These vertices can be responsible for electrostatic repulsion with the negatively charged redox active species, $[Fe(CN)_6]^{4-\text{ or }3-}$. It is obvious that the repulsive forces should be bigger in the case of $[Fe(CN)_6]^{4-}$ and therefore Fe^{3+} in $[Fe(CN)_6]^{3-}$ might be more easily reduced. To investigate this feature more properly we used the dithiol derivative 4, which possesses a dipole moment of approximately the same absolute value as 2 but of an opposite direction; from top to surface. This monolayer has its more electropositive part facing the electrolyte solution and it may rather attract both ferro-ferry cyanide redox species. Therefore, it behaves qualitatively the same as the bare Au-electrode. The only difference is that the redox currents are slightly decreased.



Figure 17. Cyclic voltammetric current response vs. applied potential for bare gold film (dashed lines), gold film modified with 2 (upper picture - solid line) and gold film modified with 3 (lower picture - solid line).

3.8 Wetting angles of water on bare gold film versus modified with the carboranethiols. Measuring of contact angles is a basic method to assess the hydrophobic or hydrophilic character of surfaces. Table 6 shows the contact angles of water on Au-films: bare and modified with **2**, **3**, or **4**, respectively. Considering the bare Au film to be hydrophobic, the **2**-SAM on Au-film caused even bigger hydrophobic character of the surface. This increase is due to the fact, that only B-H non-polar vertices are facing the water environment of the drop. The Au film with the **3**-SAM on its surface was on the contrary rather hydrophilic because of the free thiol groups that are orientated upwards. Finally, we wish to report on the wetting angle of the **4**-SAM on Au film. This contact angle was much lower than that on **2**-SAM and close to **3**-SAM on Au-films. The explanation of this observation is closely related to understanding the character of B-H and C-H vertices. C-H vertices are significantly more acidic than the B-H vertices and therefore more readily interact with

water molecules. The different wetting angles of water on **2**-SAM and **4**-SAM underline the difference between the chemical nature of B-H and C-H vertices in carborane cluster molecules.

Sample:	Bare gold film	2-SAM on	3-SAM	4-SAM
Contact angle of water	74 °	88 °	57 °	53 °

Table 6. Contact angles of water for the bare gold film and gold films with 2-, 3- and 4-SAMs.

3.9 Structural models of the species. Figure 18 shows an idealized model of the nanoparticle species. It illustrates the proposed modification of the inner space of the nanoparticles and surface coverage before and after desorption. During the synthesis some molecules of the dithiol derivative are immersed by the gold surface atoms and ultimately become incorporated into the gold cores.



Figure 18. Structural model of the studied materials (a) before and (b) after desorption of the carboranethiol derivatives from the surface of the nanoparticles.

Modification of flat surfaces is shown schematically in Figure 19. Part (a) is an illustration of the **2**-modified surface that fits all evidence gained from the structural characterization experiments. Part (b) shows the molecules of **3** bound to the flat surface by only a single thiol group. The geometrical reasons of this arrangement are obvious from the previous discussion.



Figure 19. Structural model of the gold films with surface modified with (a) 2 and (b) 3.

3.10 Gold single-crystal micro-plates and micro-wires. Experiments on the colloidal assemblies described in this report were conducted on (111) surfaces of gold single crystals (Figure 20A) that can be mechanically manipulated using a micro-manipulator. The shapes of the vast majority of the crystals prepared according to the procedure in the Experimental section can be described as triangular or hexagonal micro-plates 10 to 80 μ m large and only a few hundred nanometers thin. Figure 20C shows some of the micro-plates from a side-on view and is a good indicator of their thickness. The atomic force microscope (AFM) revealed very good flatness of the gold crystal micro-plates (Figure 22). A few step edges parallel to the edge of the crystal were observed (Figure 22B). Contrarily, many grains were observed on the surface of a flame-annealed gold film on a glass substrate using both AFM and SEM; the SE micrograph is shown in Figure 20D. The observed contrast of the grains is due to their different orientations. A part of the micro-crystallites ($\sim 5 - 10$ %) produced using 1,5-pentanediol as solvent can be described as gold micro-wires (Figure 20E). These wires were observed to grow also from the vertices of the crystal micro-plates (Figure 20F). The diameter of the wires is $\sim 0.5 \,\mu$ m and their length is $\sim 60 - 80 \,\mu$ m.



Figure 20. SE micrograph of (A) single crystal micro-plates, (B) polyhedral crystals, (C) aggregate of the crystal plates and the polyhedral crystals, (D) a flame-annealed macroscopic film, (E) a gold wire, and (F) a gold wire grown with the crystal micro-plate.

3.11 Gold colloidal assemblies. Gold particles with an average diameter of ~ 20 nm were used to form an over-layer on a gold crystal surface pre-modified with $1,12-(HS)_2-1,12-C_2B_{10}H_{10}$. This carborane derivative is a nearly regular icosahedron with thiol groups attached to carbon vertices in *para*-positions. A molecule of this dithiol derivative should ideally bind to the gold crystal surface with only one of the thiol groups. XPS analysis of the gold crystal micro-plates modified with $1,12-(HS)_2-1,12-C_2B_{10}H_{10}$ showed two different types of sulphur atoms with mutual ratio 1:1 (Figure

23A, Table 7 - sample 2). The additional modification of the gold crystal surface with gold colloids shifts the thiolate: thiol ratio in the favour of the thiolate (Figure 23B, Table 7 – sample 3). It can only be rationally explained by forming the thiolate bonds between the free thiol groups oriented from the surface upward and the approaching gold particles. An example of scanning electron micrograph of the gold particles attached to the gold crystal surface is shown in Figure 21. The molecular junction between the gold crystal surface and a colloidal particle should form an interlayer of ~ 1.2 nm which is the theoretical length of the carborane linker, including the thiolate sulphur atoms. To visualize this molecular distance, we prepared oligomers of the gold colloidal particles according to the literature.¹³⁰ An example of a colloidal dimer with approximately the molecular distance between the particles is shown in the top right inset in Figure 21. XPS results are summarized in Table 7. The gold single-crystal micro-plates are, as prepared, stabilized by the molecules of PVP, 1,3 - propanediol and oxidation products of the solvent which also serves as a reducing agent. The measured XP spectra of the C 1s electrons resemble those of PVP. They exhibit at least three components coming from different types of carbon atoms. The first component comes from carbon atoms in C-C and C-H bonds, the second can be assigned to carbon atoms in C-N- and C-OH bonds and the binding energy of the third component is consistent with carbon atoms in N-C=O bonds. The measured values of the C 1s core level binding energies of the individual components are displayed in Table 7. The spectra of the C 1s electrons of the gold crystal microplates treated with the carboranethiol derivative still exhibit components characteristic of the first sample. This finding indicates that substitution of the molecules present on micro-plate surfaces by 1,12-(HS)₂-1,12-C₂B₁₀H₁₀ thiolated clusters does not proceed completely under the used experimental conditions. The spectrum of the C 1s electrons measured for sample 3 which is additionally modified with the gold colloids is also dominated by contributions from PVP. Consequently, we cannot exclude the possibility that a fraction of gold colloidal particles is bonded to the molecules of PVP remaining on the gold crystal surface. The XPS results obtained for the sample 4, which is a square complex of Au^{3+} with two $1,2-(S^{-})_2-1,2-C_2B_{10}H_{10}$ ligands (NBu₄) $[Au(C_2B_{10}H_{10}S_2)_2])$,¹³¹ are given in Table 7 for comparison.



Figure 21. SE micrograph of the gold colloids attached to the gold crystal surface. The inset shows HR TEM picture of an 'in solution' prepared dimer of two gold colloidal particles linked together with 1,12-(HS)₂-1,12-C₂B₁₀H₁₀.



Figure 22. AFM picture of (A) the gold colloids on a mica slide, (B) the crystal micro-plate surface modified with the colloids. (C) and (D) are height and deflection mode pictures of the colloids attached to the crystal surface.



Figure 23. XP spectra of S (2p) electrons for (A) gold crystal surface modified with $1,12-(HS)_2-1,12-C_2B_{10}H_{10}$ and (B) modified additionally with a monolayer of gold colloids.

Sample	Stoichiometry	Au 4f	B 1s	S 2p _{3/2}	C 1s
1	$N_{1.0}O_{2.2}C_{8.7}Au_{4.2}$	84.0	-	-	285.4
					286.3
					288.3
2	$B_{1.0}O_{4.6}C_{11.5}S_{0.26}N_{1.19}Au_{7.2}$	84.0	189.3	161.6	285.2
				164.2	286.2
					288.2
3	$B_{1.0}O_{2.0}C_{5.4}S_{0.27}N_{0.42}Au_{2.5}$	84.0	189.8	161.4	285.2
				163.6	286.3
					288.3
4	$B_{21.8}S_{4.0}C_{25.5}N_{1.2}Au_{1.0}\\$	86.8	189.4	162.9	284.8
					286.5

Table 7. Stoichiometry calculated from B 1s, O 1s, C 1s, S 2p, Au 4f and N 1s photoemission line intensities and measured core level binding energies (in eV).

Sample 1: Au single-crystal micro-plates stabilized with the molecules of PVP and 1,3-propanediol. Sample 2: Au single-crystal micro-plates treated with $1,12-(HS)_2-1,12-C_2B_{10}H_{10}$. Sample 3: Au single-crystal micro-plates treated with $1,12-(HS)_2-1,12-C_2B_{10}H_{10}$ and additionally with gold colloids. Sample 4: NBu₄ [Au(C₂B₁₀H₁₀S₂)₂]

CHAPTER FOUR CONCLUSION

In conclusion, important data on the structure, bonding and properties of gold surfaces modified by selected carboranethiol molecules were recorded and analyzed. The carboranethiolate modified gold materials are extraordinarily stable towards oxidation and heating. There was not any change observed in the XP spectra even after several months of exposure to air. The nanoparticle gold surface is densely covered with carboranethiol molecules, and a comparison of the experimental density with the theoretical arrangement of carborane clusters on a flat surface is in a good agreement. The process of desorption indicates that the carborane molecules escape mostly as $1,2-C_2B_{10}H_{10}$ fragments leaving the sulphur atoms on the gold surface. An evidence to suggest a very interesting phenomenon consisting of the incorporation of the carborane clusters into the gold nanoparticles was observed and a structural model for the prepared materials was proposed. The prepared monolayers of $1,2-(HS)_2-1,2-C_2B_{10}H_{10}$ and $9,12-(HS)_2-1,2-C_2B_{10}H_{10}$ represent organized monolayers of dipoles with approximately the same value but opposite direction. Gold single crystal micro-plates and micro-wires were synthesized. Their dimensions enable easy mechanical manipulation. Gold colloids can be assembled on their facets and form an over-layer linked to the surface via $1,12-(HS)_2-1,12-C_2B_{10}H_{10}$ molecules. High thermal stability of the icosahedral $C_2B_{10}H_{12}$ derivatives provides a possibility to use them in electronic elements that can be temperature stressed.

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OUTPUTS

ARTICLES "A study of gold colloids assembled on gold (111) single crystal surfaces via 1,12-(HS)₂-1,12-C₂B₁₀H₁₀" Baše, T.; Bastl, Z.; Šlouf, M.; Murafa, N.; Šubrt, J.; Plešek, J.; Londesborough, M.G.S.; Kříž, O. Surface Science, in press.

"Carboranethiol-modified Gold Surfaces. A Study and Comparison of Modified Cluster and Flat Surfaces." Baše, T.; Bastl, Z.; Plzák, Z.; Grygar, T.; Plešek, J.; Carr, M. J.; Malina, V.; Šubrt, J.; Boháček, J.; Večerníková, E.; Kříž, O. Langmuir **2005**, 21, 7776.

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